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Effect of Different Concentrations of Titanium Oxide (TiO₂) on the Crystallization Behavior of Li₂O-Al₂O₃-SiO₂ Glasses Prepared from Local Raw Materials

Omar A. Al-Harbi, Emst M.A. Hamzawy and M. Mujtaba Khan
1King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia
2National Research Center, Department of Glass Research, P.C. 12622, Cairo, Egypt

Abstract: Lithium Aluminum Silicate (LAS) glasses produced from local raw materials (white silica sand and clay) and Li₂CO₃ were nucleated by different concentrations of TiO₂ to transform into glass-ceramics. Studies were performed using Differential Thermal Analysis (DTA), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Dilatometer. Addition of TiO₂ affected phase evolution, morphology and formation of β-spodumene along with brookite and Al₂TiO₅ phases. The SEM micrographs of the heat-treated glass samples also reflected bulk crystallization. However, softness of crystal edges took place on samples subjected to multi-stage heat-treatment. This may attributed to partial melting of the pre-developed phases. The CTE values were low to medium with the formation of β-spodumene and brookite, but were high with the formation of Al₂TiO₅ and amorphous phases in addition to both the β-spodumene and brookite phases. The values of low, medium and high Coefficient of Thermal Expansion (CTE) ranged between 3.02-49.672×10⁻⁷ °C⁻¹ in the double and -2.171-31.737×10⁻⁷ °C⁻¹ in the multi-stage heat treatments with in a temperature range of 25-300°C.

Key words: White silica sand, glass ceramics, crystallization, TiO₂, β-spodumene, brookite, thermal expansion coefficient

INTRODUCTION

Although, lithium-aluminum-silicates based glass-ceramics have been studied for decades but still it remains a challenge for scientists to improve or modify its properties. The Li₂O-Al₂O₃-SiO₂ glass-ceramics of low thermal expansion coefficient are considered as primary requirements of many industrial sectors. The characteristics of the glass-ceramics depend on the nature of crystalline phases and the microstructures. Earlier investigations have successfully utilized primarily raw materials to prepare different type of glass-ceramics by using locally available raw materials and produced lithium aluminium silicates based glass-ceramics of low coefficient of thermal expansion (Omar et al., 1986; Khater, 1987; El-Shennawi et al., 1998; Hamzawy, 1992; Kauffman and Dyk, 1993; Idris and Khater, 2004; Al-Harbi and Khan, 2008). Stookey (1960) reported that TiO₂ is the most common nucleating agent in the glass-ceramics. It is also recognized as one of the best nucleating agents in the fabrication of Li₂O-Al₂O₃-SiO₂ (LAS) glass-ceramics by conventional melting and crystallization process (Bash, 1995). Barry et al. (1970) reported that TiO₂ acts as a surfacial active agent and increases the nucleation rate in the Li₂O-Al₂O₃-SiO₂ system. Titania nucleated glass-ceramics in the Li₂O-Al₂O₃-SiO₂ type having a thermal expansion coefficients less than 15×10⁻⁷ °C⁻¹ and in some cases approaching zero, were produced (McMillan, 1979). The amount of TiO₂ in various types of glass-ceramics ranged from 2-20% on weight basis (McMillan, 1979). When used in large amounts, TiO₂ becomes a major part of glass composition. Zdanewski (1978) suggested that TiO₂ decreases the viscosity of the base glasses at high temperature which is favorable for nucleation and growth of the main crystalline phase. The TiO₂ is soluble in a wide range of molten glasses. But during cooling or subsequent reheating, large numbers of submicroscopic particles are precipitated and these apparently assist the development of major crystal phases from the glass (McMillan, 1979). The objective of the present study is to determine the possible role of TiO₂ in the Li₂O-Al₂O₃-SiO₂ glass on characteristics such as thermal behavior, crystallization, microstructures and the coefficient of thermal expansion.

MATERIALS AND METHODS

The study was carried out at Geology Research Laboratory, National Center for Water Research (NCWR), King Abdulaziz City for Science and Technology (KACST), Riyadh during 2008.

Corresponding Author: Omar A. Al-Harbi, National Center for Water Research, King Abdulaziz City for Science and Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia
Table 1: Chemical composition of the starting raw materials

<table>
<thead>
<tr>
<th>Oxides (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>FeO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock</td>
<td>98.89</td>
<td>0.27</td>
<td>0.21</td>
<td>0.02</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>White silica sand</td>
<td>94.32</td>
<td>37.1</td>
<td>0.78</td>
<td>0.07</td>
<td>0.03</td>
<td>0.23</td>
<td>0.19</td>
<td>3.74</td>
<td></td>
<td>14.1</td>
</tr>
</tbody>
</table>

Table 2: Chemical composition of the glass batches in oxide form (weight basis %)

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>TiO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA3 base</td>
<td>55.54</td>
<td>34.97</td>
<td>0.77</td>
<td>0.03</td>
<td>0.22</td>
<td>0.18</td>
<td>4.62</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>LST1</td>
<td>53.82</td>
<td>33.88</td>
<td>0.74</td>
<td>0.03</td>
<td>0.22</td>
<td>0.18</td>
<td>4.47</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>LST2</td>
<td>52.20</td>
<td>32.86</td>
<td>0.72</td>
<td>0.03</td>
<td>0.21</td>
<td>0.17</td>
<td>4.34</td>
<td>0.84</td>
<td></td>
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<tr>
<td>LST3</td>
<td>50.67</td>
<td>31.90</td>
<td>0.70</td>
<td>0.03</td>
<td>0.20</td>
<td>0.17</td>
<td>4.21</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>LST4</td>
<td>49.23</td>
<td>30.99</td>
<td>0.68</td>
<td>0.03</td>
<td>0.20</td>
<td>0.16</td>
<td>4.09</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>LST5</td>
<td>47.87</td>
<td>30.13</td>
<td>0.66</td>
<td>0.03</td>
<td>0.19</td>
<td>0.16</td>
<td>3.98</td>
<td>1.66</td>
<td></td>
</tr>
</tbody>
</table>

Preparation of base glass samples: Locally available white silica sand and clay with Li₂CO₃ (Commercial Grade Reagents) and TiO₂ were used as the starting materials. The TiO₂ was added at the rate of 0, 3, 6, 9, 12 and 15 g per 100 g of glass oxide. A base glass batch with sequential additions of TiO₂ concentrations was prepared for the experiment. The chemical analysis of the raw materials used in the experiment is shown in Table 1. The chemical composition of prepared glasses is shown in Table 2. The prepared base glass batch was mixed well by the Ball Mill, then transferred into sintered aluminum crucibles and placed in the Molybdenum silicide furnace at temperatures ranging from 1350-1450°C for 2 h. The glass melt was stirred at an interval of half an hour for homogenization during the whole process. A bubble-free glass melt was poured into preheated steel casting molds as rods and patters. Later on, the glass melt was transferred to a preheated muffle furnace at 600°C for annealing.

Sample characterization: About 30 mg of the powdered sample (between 25-50 μg grain sizes) was used for DTA analysis by A Shimadzu DTG-60H micro Differential Thermo Analyzer. The Al₂O₃ powder was used as a reference material. A heating rate of 10°C min⁻¹ was maintained for all the DTA tests. A double and a multi-stage heat-treatment schedule were followed the DTA temperature peaks. The glass samples were heat-treated between 780-1050°C for 2 h in the double and multi-stage schedule. The powdered samples were tested to identify the crystallized phases using Mini Flex of Rigaku-Japan, adopting Ni-filtered Cu-radiation. The JCPDS diffraction file Cards (2001) were used as reference data for the interpretation of X-ray patterns obtained in this study.

The microstructures and the crystal growth of some heat-treated gold coated glasses were examined by SEM using Joel-JSM-8800, Japan. The dimensional changes occurring with the change of temperature, were measured by a NETZSCH DIL 402 PC-Germany Instrument. The CTE of prepared samples was measured with a dimension of 0.5×0.5×2.0 cm² at a heating rate of 5°C min⁻¹.

RESULTS AND DISCUSSION

The DTA data showed that the crystallization temperature of LA-3 base glass (without nucleating agents) were at 918 and 963°C and the intensity of peak was also high (Table 1). The effect of batch composition on the crystallization of glass showed that the presence of small amount of TiO₂ in batch composition changed the rate and phase of crystallization as well as the viscosity of the resultant glass melt. Similar to TiO₂, Al₂O₃ also reduced the melting point and improved crystallization. The Al₂O₃ ion can be four or six-co-ordinate with oxygen giving rise to tetrahedral Al₂O₃ or octahedral Al₂O₃ groups. The tetrahedral group can replace SiO₂ tetrahedral in silicate lattices to give the different arrangements. Most of the earlier workers (Das and Douglas, 1967; Omar et al., 1971; Shennawi et al., 1991) agreed that Al₂O₃ as well as the SiO₂ ion were effective in increasing the viscosity of the glass melts by forming polymer units between Al₂O₃ and SiO₂ tetrahedral groups.

Weak transition temperatures (TG) were observed in the fabricated glasses ranging from 709 to 740°C (Fig. 1). The endothermic peaks characters were almost identical in the temperature of 709-740°C. The low intensity of Tg peak was due to slow rate of glass melt cooling (Mazarin and Garkin, 2007). Other than LA3-T1 and LA3-T2 samples, the exothermic peaks were sharp in the temperature range of 914-916°C. However, in comparison to base glass the intensity of peaks was proportional to the increasing concentration of TiO₂ compared to LA3, LA3T-3 and LA3-T5 samples (Fig. 1). In comparison to the parent glass, the exothermic peak temperatures either decreased or increased according to the TiO₂ ratios. In LA3-T1 (containing ~3% TiO₂) and LA3-T2 (containing ~6% TiO₂) glasses, the decrease in exothermic temperature took place by about 50 and 100°C, respectively (Fig. 1). This is in agreement with El-Shennawi et al. (1998), who considered that addition of TiO₂ acted as a nucleating agent. But when the concentration of TiO₂ increased to 9% (as in LA3-T3) and 12% (LA3-T4) and 15% (LA3-T5) in glass samples, the exothermic peaks were almost identical to the base glass (LA3). McMillan (1979) used TiO₂ in various types of glass-ceramics ranging from 2-20% (on weight basis) and observed that when TiO₂ is used in high concentrations, it becomes a major part of the glass composition. Barry et al. (1970) reported that TiO₂ acts as a surfacial
active agent and increases the nucleation rate in the Li₂O-Al₂O₃-SiO₂ system. Morsi and El-Shennawi (1983) indicated that little amount of TiO₂ was more effective to enter into network forming positions than into network modifying positions. Sandstrom et al. (1980) reported that >4 g TiO₂ probably acts in reverse. However, in the present study, the DTA traces showed that LA3 base glass and other samples having TiO₂ concentration of 6% and above have almost identical exothermic peaks. These exothermic peaks were associated with the crystallized lithium-aluminum-silicate phases.

β-Spodumene, brookite and aluminum titanium oxide (Al₃TiO₇) phases were developed through out the different heat-treatment schedule (Fig. 2, 3). In both the double and multiple-stage heat-treatments of Li₂O-Al₂O₃-SiO₂-TiO₂ system, there was no significant difference in the crystallization of β-spodumene and brookite phases (Table 3). However, in the multi-stage heat-treatment, the crystallization of titanium oxide (Al₃TiO₇) as well as an increase in the intensity of XRD peaks took place (Fig. 2, 3). In the Li₂O-Al₂O₃-SiO₂ system, the literature proved that the crystallization of titnate is an independent phase (Bae et al., 2005) here, while others assured the formation of Al₃TiO₇, as a primary or micro-separated phase with TiO₂ acting as a nucleating agent (4 mole %) (Beall and Duke, 1983).

The heat-treatment of the present glasses and the base glass containing parent TiO₂, showed that low ratios of TiO₂-containing samples acted mainly as nucleating agent. On the contrary, high ratio of nucleating agent not only acted as a catalyst but also as dependance developed phases along with the main phases. The double heat treatment in the case of LA3-T1 and LA3-T2...
samples indicate that the crystallization does not take place below 900°C and resulted in an amorphous phases.

Almost homogenous bulk crystalline glass-ceramics of major β-spodumene with brookite and may with Al₂TiO₅ were developed (Fig. 4a-d). The examination of SEM photographs showed the roughness and softness of the crystal edges that characterized the double and multi-stage glass-ceramic samples, respectively (Fig. 4). This may be attributed to the increase of temperature that lead to partial melting and an increase in glass quantity and frequently the softening of grain edges. However, the major β-spodumene may be observed as subhedral tetragonal crystals and might be modified into subhedral six-sided crystals. The presence of TiO₂ in both forms (as brookite and Al₂TiO₅) helped in the bulk crystallization of glass. As also, the mechanism showed the development of these phases as early as glass in glass phase's separation or formation of such heterogeneous TiO₂ containing phases and at high temperature epitaxial crystallization took place.

The Coefficient of Thermal Expansion (CTE) in the present glass-ceramic samples were affected by heat-treatment, developed phases, size and orientation of grains and residual glasses (Table 4, Fig. 5, 6). Through the heat-treatment schedule, the developed crystalline phases were β-spodumene with brookite and Al₂TiO₅ that gave CTE values between 3.02-49.67×10⁻⁷ °C⁻¹ and 22.709-58.356×10⁻⁷ °C⁻¹ in the double stage and between -2.171-31.737 and 16.986-33.150×10⁻⁷ °C⁻¹ in multi-stages

Fig. 3: XRD patterns for the glasses heat-treated in multi-stage heat treatments, S: β-spodumene, B: Brookite, At: Aluminium titanium oxide Al₂TiO₅

Fig. 4: SEM micrographs of LA3-base-LA3-T5 glasses heat-treated in double and multi-stage heat-treatment, (a) LA3-base 780°C/2 h-916°C/3 h, (b) LA3-base 780°C/2 h-916°C/3 h-970°C/3 h, (c) LA3-T5 780°C/2 h-916°C/3 h and (d) LA3-T5 780°C/2 h-916°C/3 h-970°C 3 h
The LA3 base glass subjected to crystallization at double and multi-stage recorded the lowest CTE values between 8.699-22.988 and -2.171-16.986\times10^{-5} \, ^\circ\text{C}^{-1} at a temperature range of 25-500^\circ\text{C}, respectively. This suggests that the crystallization of β-spodumene along with brookite gave the lowest CTE values. Furthermore, the incorporation of TiO_2 and the formation of amorphous phases after double heat treatment increased the CTE values up to 49.672 (25-300^\circ\text{C}) and 58.356\times10^{-7} \, ^\circ\text{C}^{-1} (25-500^\circ\text{C}), respectively. This may be ascribed to the increase of glassy phase as well as in the double stage heat-treatment that are crystalline free samples, which were characterized by the formation of Al_2TiO_5 phase in addition to β-spodumene and brookite. The CTE values of high TiO_2 containing samples (LA3-T3 and LA3-3-T5) along with the formation of β-spodumene and brookite were medium ranging from 3.020-20.279\times10^{-7} \, ^\circ\text{C}^{-1} (25-300^\circ\text{C}) and 22.709-58.356 (25-500^\circ\text{C}) in the double stage, whereas it ranged from 14.392-20.612 (25-300^\circ\text{C}) and 25.205-28.362\times10^{-7} \, ^\circ\text{C}^{-1} (25-500^\circ\text{C}) in multi-stage heat-treatment.

In general, according to the developed phases, the CTE values were low to medium in TiO_2 free addition in presence of β-spodumene and brookite. Whereas, the CTE values were high with the formation of Al_2TiO_5 in addition to β-spodumene and brookite.

**CONCLUSION**

The characteristics of glass-ceramics in the Li_2O-Al_2O_3-SiO_2-TiO_2 system depended on the sequential addition of TiO_2 and the heat-treatment parameter crystalline. The β-spodumene, brookite and Al_2TiO_5 were the developed phases during different heat treatment schedule. The low TiO_2 ratios in the samples acted mainly as a nucleating agent. But at high TiO_2 ratios, it acted as a nucleating agent and as a dependent phase that can be considered along with the developed main phases. Bulk crystalline materials were developed during glass fabrication process. The softness of the crystal edges in the multistage heat-treatment was due to the increase of glassy phase due to partial melting of pre-developed phases. The CTE values were low to medium with the formation of β-spodumene and brookite, but were high with the formation of Al_2TiO_5 and amorphous phases in addition to both the β-spodumene and brookite phases.

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